

THERMOMECHANICAL MODEL OF HYDRATION SWELLING IN SMECTITIC CLAYS: I TWO-SCALE MIXTURE-THEORY APPROACH

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SUMMARY

A thermomechanical theory of hydration swelling in smectitic clays is proposed. The clay is treated as a three-scale swelling system wherein macroscopic governing equations are derived by upscaling the microstructure. At the microscale the model has two phases, the disjoint clay platelets and adsorbed water (water between the platelets). At the intermediate (meso) scale (the homogenized microscale) the model consists of clay particles (adsorbed water plus clay platelets) and bulk water. At the macroscale the medium is treated as an homogenized swelling mixture of clay particles and bulk-phase water with thermodynamic properties defined everywhere within the macroscopic body. In Part I, the mesoscopic model governing the swelling of the clay particles is derived using a mixture-theoretic approach and the Coleman and Noll method of exploitation of the entropy inequality. Application of this procedure leads to two-scale governing equations which generalize the classical thermoelastic consolidation model of non-swelling media, as they exhibit additional physico-chemical and viscous-type terms accounting for hydration stresses between the adsorbed fluid and the clay minerals. In Part II the two-scale model is applied to a bentonitic clay used for engineered barrier of nuclear waste repository. The clay buffer is assumed to have monomodal character with most of the water essentially adsorbed. Further, partial results toward a three-scale thermomechanical macroscopic model including the bulk phase next to the swelling particles are derived by homogenizing the two-scale model with the bulk water. A notable consequence of this three-scale approach is that it provides a rational basis for the appearance of a generalized inter-phase mass transfer between adsorbed and bulk water. Copyright © 1999 John Wiley & Sons, Ltd.

Key words: swelling clay; mixture theory; physico-chemical effects; second law of thermodynamics; internal variables

1. INTRODUCTION

Swelling porous media such as 2-1 lattice clays, hydrophilic polymers and shales are ubiquitous in many aspects of life. For example, in foundation engineering the clay soil swells and heaves upward causing damage to the foundations of buildings, bridges, highways, and runways. In oil and gas production swelling shales consists of 75 per cent of drilled formations and have been responsible for 90 per cent of wellbore instability problems. The response of bentonitic-based compacted swelling clays under thermomechanical effects has received great attention in recent years because of their use as sealing materials to inhibit the migration of contaminants from

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hazardous wastes to the environment. In the case of nuclear heat-generating wastes, canisters of vitrified radioactive waste are buried in compacted clay which act as a geochemical filter for the migration of radionuclides to the groundwater flow. The canisters form the short-term barrier system, while the clay barrier provides the long-term protection against contamination.

The influence of thermal effects on the analysis of swelling materials is crucial since their properties may drastically change with temperature (e.g. the permeability of the clay). The heating of compacted bentonitic clays used for barriers may lead to expansion and cracking and thus enhance the migration of radionuclides to the ground water leading to unacceptable conditions for the barrier. Other applications of the coupling between mechanical and thermal effects appear in enhanced oil recovery technology, extraction of energy from pressurized geothermal reservoirs and consolidation of soils under furnace foundations. As such, it is imperative that any mathematical model used to determine the thermomechanics of clay contain the appropriate constitutive relations to account for the swelling nature of these systems.

Thermomechanical models for granular non-swelling porous media (e.g. rock or sandstone) have been widely discussed in the literature (see e.g. References 1–3). Unlike non-swelling systems, whose thermoelastic theories assume non-interacting bulk-phase water, the thermomechanics of swelling clays is somewhat different. The constitutive behaviour of colloidal systems, such as highly swelling clays (bentonite and montmorillonite) is strongly dictated by the solid–fluid physico-chemical interaction. Physico-chemical forces have at least three components: the Van der Waals attraction, electrostatic (or osmotic) repulsion and surface hydration (a structural component, see e.g. Reference 4). Physico-chemical interactions perturb the properties of the water in the interlamellar spaces.⁵ Consequently, four different types of water survive in this scenario (see e.g. References 6 and 7): (i) free, or bulk water lying in porous openings and whose properties are not significantly affected by the presence of clay minerals; (ii) structural immobile water, composed of ordered water molecules which arrange themselves in layers parallel to the clay surface (usually less than 10 fluid monolayers or 25 Å). Due to its inhomogeneous and anisotropic character and high viscosity, the structural water is able to support shear stresses at equilibrium and exhibits solid-like behaviour;⁸ (iii) mobile adsorbed or vicinal water lying in the interlamellar and interparticle spaces, provided $10 < h < 30$ monolayers. In this range of moisture content the adsorbed fluid exhibits fluid-like behaviour and can withstand a normal hydrostatic pressure but not shear stresses at equilibrium. Microscopically, the mobile adsorbed phase is viewed as a thin liquid film coating the mineral surfaces. The hydrodynamics and thermodynamics of thin liquid films has been developed by Derjaguin and coworkers⁹ who described the lyophilic interaction between the film and surface in terms of a *disjoining pressure*, defined as an excess in film pressure relative to the surrounding bulk phase. Several different methods have been employed at the microscale to incorporate hydration effects in the film equations of motion (see e.g. body force approach).¹⁰ In contrast to bulk fluids, whose flow is governed by pressure gradients, the hydrodynamics of thin liquid films is mainly dictated by the gradient of the disjoining pressure who provides an additional driving force for thin film flow (see e.g. Reference 11).

Clusters of clay platelets when hydrated form ‘particles’ consisting of an assemblage of stacked silicate layers and adsorbed water. These particles swell under hydration and shrink under desiccation. Experimental evidence indicates that for interstices smaller than 50 Å, swelling is due primarily to hydration forces and diffusion double-layer forces are believed too weak to explain the anomalous behaviour of the adsorbed water (see References 5, 4, 13). The averaged counterpart of the disjoining pressure, is the *swelling pressure*, defined as an overburden pressure excess

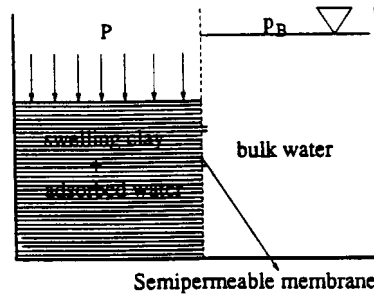


Figure 1. Low's swelling pressure experiment

that must be applied to a saturated mixture of clay and adsorbed water to keep the layers from moving apart.¹³ Figure 1 depicts a classical reverse osmosis swelling pressure experiment wherein bulk water is separated from an ordered clay-adsorbed water mixture by a semipermeable membrane. Due to hydrophilicity the clay tends to swell on imbibition by forcing its layers apart. In this experiment an overburden pressure P is applied normal to the clay-water mixture and the average interlayer separation, λ , of the platelets is measured by X-ray diffraction. The difference between the overburden and the bulk pressures p_B is the swelling pressure Π

$$\Pi \equiv P - p_B \quad (1)$$

Considering $p_B = p_{\text{atm}}$, with p_{atm} denoting the atmospheric pressure, Low examined the equilibrium swelling pressure of different montmorillonites saturated with adsorbed water and found that the dimensionless swelling pressure (Π/p_{atm}) satisfies the empirical relation

$$\Pi + 1 = \exp\left(\alpha\left(\frac{1}{e} - \frac{1}{e^*}\right)\right) = B \exp\left(\frac{a}{e}\right) \quad (2)$$

where e denotes the void fraction $e \equiv \phi_1/(1 - \phi_1)$ (ϕ_1 denotes the volume fraction), e^* is the void fraction when $\Pi = 0$ (when $P = p_B$), α is a constant related to the specific surface area and cation exchange capacity and $B = \exp(-\alpha/e^*)$. In the above relation the adsorbed water is assumed incompressible and the notation Π for the dimensionless swelling pressure has been maintained.

The effects of temperature on physico-chemical stresses have also been discussed in the literature. Zhang *et al.*¹⁴ analysed the influence of thermal effects on the swelling pressure and observed a slight decrease of Π with T and that interlayer spacings are quite insensitive to changes in T for fixed Π . Baldi *et al.*¹⁵ have shown that the effective thermal expansion of the adsorbed water is higher than that of bulk water at low temperatures. Dehydration of the adsorbed water due to heating and its release of the interlamellar spaces is a widely accepted phenomenon which has been verified experimentally (see e.g. Reference 16). As temperature increases the mobility of the adsorbed water increases and it gradually becomes free water. Consequently, the adsorbed water release of the interlamellar spaces leads to a mass transfer process. This thermally induced adsorbed water degeneration has been modeled within a framework of the mixture theory by Ma and Hueckel.¹⁷⁻¹⁹ In this framework the adsorbed water is considered immobile and the mass transfer arises as a phenomenological concept of interconstituent mass exchange appearing as a source term in the fluid mass balances, depending linearly on temperature rate.

An alternative procedure to derive macroscale governing equations for thermomechanical processes in porous media can be pursued by a rigorous upscaling of the microstructure behaviour. Approaches based on this technique include mixture theory and methods which propagate microscopic governing equations to the larger scale (e.g. homogenization, volume averaging, etc.). Hybrid Mixture Theory (HMT) (see References 20–21) consists of classical mixture theory in the sense of Bowen⁸ applied to a multiphase system with volume-averaged balance equations. In a medium with M phases an average value for each phase property is established at every point in the mixture, forming M coexisting continua. These equations are defined everywhere so that the microscopically distinct phases are now viewed as superimposed continua with each averaged variable defined precisely in terms of its microscopic counterparts. For media with negligible interfacial effects, HMT reproduces the balance laws postulated in classical mixture theory. In both of these formulations constitutive equations are developed on the averaged scale by exploiting the entropy inequality using the Coleman and Noll method.²³ Constitutive equations for swelling porous media have also been developed within the framework of the mixture theory by Hueckel,⁷ Ma and Hueckel,¹⁷ Karalis²⁴ and Eringen.²⁵ More recently, using a non-equilibrium thermodynamics approach Heidug and Wong²⁶ developed a generalized Biot's theory of poroelasticity which incorporates perturbations in the pore fluid's chemistry due to physical–chemical interaction.

A common fact inherent to these aforementioned approaches is that adsorbed water and clay minerals are combined to form one single solid phase; *the clay particle*, referring to as a cluster of clay minerals tightly bound together by absorbed water. Here we pursue the generalization of these approaches aiming at deriving two-scale and three-scale models capable of incorporating the adsorbed water mobility within the clay particles and thus obtain a more accurate description of swelling. As mentioned before, adsorbed water can exist in three different states, each one exhibiting a different constitutive behaviour. The derivation of a macroscopic model with a detailed level of accuracy capable of incorporating each particular feature of the microstructure is an overwhelming task and out of scope of this work. Instead, we pursue a unified thermodynamical treatment for the different forms of adsorbed water. In this procedure, we establish a thermodynamical basis for a modified Terzaghi's effective stress principle for swelling systems in which we refer to as *adsorbed water*, fluid whose thermodynamic state is affected by the proximity of the mineral surfaces. This includes 1–10 layers of immobile water and also the other portion of mobile water. Subsequently, when deriving the hydrodynamics of the adsorbed water, we concentrate our analysis on the thermodynamics of the mobile phase and consider the immobile phase as part of the solid.

A two-scale HMT model denotes the thermodynamical approach for a two-phase swelling system composed by the solid phase and adsorbed water (see Reference 27). Within the same context, the modelling of *three-scale swelling systems* (i.e. porous media composed of swelling porous particles and bulk fluid (water unaffected by the solid phase) requires an additional upscaling. A three-scale picture (micro, meso and macro) of a swelling porous matrix is depicted in Figure 2. At the microscale the model has two phases, the disjoint clay platelets and the adsorbed water. At the mesoscale (the homogenized microscale) the model consists of the clay particles and bulk water. A *three-scale model* denotes the approach developed at the macroscale wherein the bulk water is homogenized with the mesoscale swelling particles. To propagate information between scales, several upscaling methods can be used. In References ^{28–30}, HMT is used to upscale the microscale to the mesoscale and the homogenization procedure³¹ to upscale the mesoscopic governing equations to the macroscale. Application of these two levels of

averaging lead to an isothermal model resembling in form the so-called *dual porosity* or *distributed models with microstructure* (see Reference 32). This type of model has been successfully used to describe naturally fractured reservoirs in which the system of fractures play the role of the bulk system (where the macroscopic flow takes place) and the matrix blocks behave as the analogue to the clay particles which are treated as sources/sinks to the bulk phase.

In this work we pursue the generalization of the approach of Murad *et al.*^{28–30} by deriving two-scale and three-scale models for swelling clays capable of capturing the coupling between thermal and physicochemical effects. In Part I a two-scale thermomechanical model is derived within the framework of HMT and the Coleman and Noll method of exploitation of the entropy inequality. In the linear case we show that, the two-scale governing equations possess a structure similar to those governing thermoelastic consolidation of non-swelling media but exhibit additional physico-chemical and viscous-type terms accounting for the thermo-physico-chemical interaction between the adsorbed fluid and the clay minerals. In Part II, the two-scale model is applied to a bentonitic clay used for engineered barrier of nuclear waste repository and some partial three-scale results are derived (such as a generalized mass transfer function between adsorbed and bulk fluids) from a rigorous homogenization of the microstructure.

In what follows we discuss two main assumptions underlying the theory developed herein, namely: (i) A monomodal distribution for the clay buffer is considered wherein most of the water essentially adsorbed. This assumption is based on the results of Pusch and Carlsson,³³ who showed that, in contrast to loose clays, a very small fraction of bulk-phase water survives in highly compacted bentonites (density larger than 1.8 t/m^3), where the clay is characterized by a parallel arrangement of platelets with face-to-face contacts. On the other hand, the results of Pusch and Hokmark³⁴ also show that, even for very dense smectitic clays, after water uptake, free or bulk water still remains in some narrow zones. Furthermore, Pusch and Hokmark³⁴ presented results illustrating that dense clays are characterized by an homogeneous structure with very low uniform bulk-phase percolation rates in the narrow zones (in contrast to soft clays where the percolation rates are at least 100 times higher than in denser clays). Based on this, we neglect the bulk water flow in the clay buffer application and consider that the two-scale model provides an accurate portrait of the influence of hydration forces on the overall performance of the bentonitic clay. (ii) In addition, we also assume that physico-chemical forces are due primarily to hydration forces. The exchangeable cations are condensed on the clay surface, i.e., they are concentrated in the Stern layer, in such a way that the negative surface charge is effectively screened. In other words, following Low⁵ surface hydration is the dominant component of swelling and the charge of the clay contributes only weakly to the swelling pressure.

2. TWO-SCALE THERMOMECHANICAL MODEL

We begin by modelling the clay particles at the mesoscale as an homogenized two-phase system composed of clay platelets and adsorbed water with averaged properties defined everywhere within the particle domain. The mesoscopic definition of each field variable in terms of its microscopic counterpart can be found in Hassanizadeh and Gray.²¹ Following the usual framework of mixture theory consider a mixture of two liquid–solid coexisting continua which undergo independent motions $\mathbf{x} = \mathbf{x}_\alpha(\mathbf{X}_\alpha, t)$, $\alpha = 1, s$ with respect to each reference configuration (here \mathbf{x} denotes the spatial position of the particle of the α -phase at time t with respect to a reference position \mathbf{X}_α). For simplicity assume that interfaces contain no thermodynamic properties, entropy fluxes are solely due to heat fluxes and the solid and fluid are non-polar,

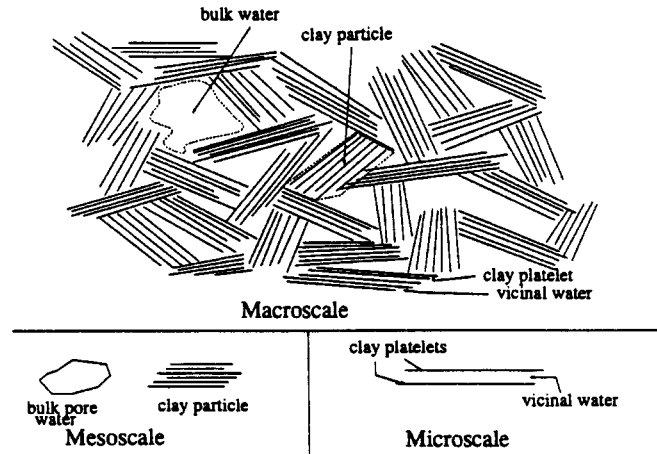


Figure 2. Three-scale model for clay

non-reacting phases in local thermal equilibrium. This latter assumption allows to assign a local common temperature T for both phases. In addition, assume that all external sources except the one appearing in the energy equation (heat supply) are negligible. The local mesoscopic mass, momentum, energy and entropy equations are given by (see Reference 21)

Conservation of mass:

$$\rho_\alpha \frac{D_\alpha \phi_\alpha}{Dt} + \phi_\alpha \frac{D_\alpha \rho_\alpha}{Dt} + \phi_\alpha \rho_\alpha \operatorname{div} \mathbf{v}_\alpha = 0, \quad \alpha = 1, s \quad (3)$$

where ϕ_α , ρ_α and \mathbf{v}_α are, respectively, the volume fraction, intrinsic volume-average density, and mass-average velocity of phase α . D_α/Dt is the material time derivative following the α -phase

$$\frac{D_\alpha}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}_\alpha \cdot \nabla \quad (4)$$

Conservation of momentum:

$$\phi_\alpha \rho_\alpha \frac{D_\alpha \mathbf{v}_\alpha}{Dt} - \operatorname{div}(\phi_\alpha \mathbf{t}_\alpha) = \hat{\mathbf{T}}_\alpha, \quad \alpha = 1, s \quad (5)$$

where \mathbf{t}_α denotes the average symmetric stress tensor for phase α and $\hat{\mathbf{T}}_\alpha$ is the exchange of momentum to phase α from the other phase.

Conservation of energy:

$$\phi_\alpha \rho_\alpha \frac{D_\alpha E_\alpha}{Dt} - \phi_\alpha \operatorname{tr}(\mathbf{t}_\alpha \mathbf{d}_\alpha) + \operatorname{div}(\phi_\alpha \mathbf{h}_\alpha) - \phi_\alpha \rho_\alpha \hat{H} = \hat{Q}_\alpha, \quad \alpha = 1, s \quad (6)$$

where E_α is the average internal energy density of phase α , \mathbf{d}_α is the symmetric part of $\nabla \mathbf{v}_\alpha$, \mathbf{h}_α is the heat flux, and \hat{Q}_α and \hat{H} are the net exchange of energy between phases and external heat supply, respectively.

Entropy inequality

$$\Lambda = \sum_{\alpha=1,s} \left[\phi_\alpha \rho_\alpha \frac{D_\alpha \eta_\alpha}{Dt} + \operatorname{div} \left(\frac{\phi_\alpha \mathbf{h}_\alpha}{T} \right) - \left(\frac{\phi_\alpha \rho_\alpha \hat{H}}{T} \right) \right] \geq 0$$

where η_α is the entropy of phase α per unit mass of the mixture, T is the temperature assumed locally equal for both phases and Λ is the rate of net entropy production. In addition, conservation of momentum and energy for the mixture as a whole requires

$$\begin{aligned} \sum_{\alpha=1,s} \hat{\mathbf{T}}_\alpha &= \mathbf{0} \\ \sum_{\alpha=1,s} \hat{Q}_\alpha &= - \sum_{\alpha=1,s} \hat{\mathbf{T}}_\alpha \cdot \mathbf{v}_\alpha = - \hat{\mathbf{T}}_1 \cdot \mathbf{v}_{1,s} \end{aligned} \quad (7)$$

where $\mathbf{v}_{1,s} = \mathbf{v}_1 - \mathbf{v}_s$ is the mass-average relative velocity.

A constitutive theory formulated in terms of temperature rather than entropy is usually obtained by defining the mesoscale Helmholtz free energy of the α -phase by the Legendre transform $A_\alpha = E_\alpha - T\eta_\alpha$. In terms of this potential and using (6) we can rewrite the entropy inequality as

$$T\Lambda = \sum_{\alpha=1,s} \left[-\phi_\alpha \rho_\alpha \left(\frac{D_\alpha A_\alpha}{Dt} + \eta_\alpha \frac{D_\alpha T}{Dt} \right) + \phi_\alpha \operatorname{tr}(\mathbf{t}_\alpha \mathbf{d}_\alpha) - \frac{\phi_\alpha}{T} \mathbf{h}_\alpha \cdot \nabla T \right] - \mathbf{v}_{1,s} \cdot \hat{\mathbf{T}}_1 \geq 0 \quad (8)$$

The average mesoscopic strain tensor of the solid phase \mathbf{E}_s is defined as

$$\mathbf{E}_s = \frac{1}{2}(\mathbf{C}_s - \mathbf{I}) \quad (9)$$

where $\mathbf{C}_s = \mathbf{F}_s^T \mathbf{F}_s$ with $F_s = \operatorname{grad} \mathbf{x}_s$ denoting the deformation gradient of the solid phase (with grad denoting the differentiation with respect to a material particle on the mesoscale).

Just as in classical mixture theory, constitutive restrictions are obtained by exploiting the entropy inequality in the spirit of the Coleman and Noll method.^{23,35} This guarantees that the second law of thermodynamics is not violated. In order to exploit the entropy inequality, it is necessary to identify the independent variables which dictate the constitutive behaviour of the medium. For example, for a thermoelastic solid the variables might include the strain, the temperature, and the gradient of the temperature.³⁵ For a viscous fluid, the rate of deformation tensor is included in the list of independent constitutive variables.³⁵ It should be noted that in deriving these constitutive restrictions the list of independent constitutive variables is critical. In fact, it is this list of variables which *defines* the material. Assuming that on the mesoscale, both solid and adsorbed liquid phases are compressible, and the adsorbed water is non-viscous, the behaviour of the system is dictated by the following independent variables.²⁹

$$T, \rho_s, \rho_l, \mathbf{E}_s, \nabla \mathbf{E}_s, \nabla T, \mathbf{v}_{1,s} \quad (10)$$

The novelty in the above set of independent variables is the inclusion of \mathbf{E}_s and $\nabla \mathbf{E}_s$ which implies that the mechanical behaviour of the system is partially dictated by the separation and distortion of the clay platelets and their spatial variations. The inclusion of $\nabla \mathbf{E}_s$ in the above set is crucial for a derivation of a proper form of Darcy's law for the adsorbed water. In particular the inclusion of $\nabla \mathbf{E}_s$ allows for strain-induced flow of the adsorbed water at the mesoscale (see Reference 29). In

addition ∇T is also included to allow for heat conduction. The dependent variables are

$$A_\alpha, \eta_\alpha, \frac{D_s \phi_1}{Dt}, \mathbf{t}_\alpha, \mathbf{h}_\alpha, \hat{\mathbf{T}}_1 \quad \alpha = 1, s \quad (11)$$

The reason for including the material time derivative of the volume fraction following the solid phase, $D_s \phi_1 / Dt$, as a dependent variable is due to the so-called closure issue (see Reference 36). In these constitutive variables a careful count indicates that there is still an additional unknown, the volume fraction, for which there is no corresponding equation. One way of closing the system is to postulate a rate law for $D_s \phi_1 / Dt$ (see References 36, 37).

It is usually postulated that the Helmholtz free energies of the phases depend only on a subset of the set of independent variables. For the system under consideration we postulate the dependence of the Helmholtz free energies on the following independent variables:

$$A_s = A_s(T, \rho_s, \mathbf{E}_s) \quad (12)$$

$$A_1 = A_1(T, \rho_1, \mathbf{E}_s) \quad (13)$$

The adsorbed water is distinguished from bulk water by postulating the dependence of A_1 on the proximity of the solid, i.e. $A_1 = A_1(\dots, \mathbf{E}_s)$. This allows the adsorbed liquid structure to be a function of the separation and shear strain of the solid phase. This change is represented by the strain tensor \mathbf{E}_s which, by definition, is the strain of the 'smeared out' solid phase (see Reference 38). If the thermodynamic properties of the liquid phase are not affected by the presence of the solid phase e.g. sandstone), A_1 is independent of \mathbf{E}_s and the liquid is considered a bulk fluid. By choosing the above constitutive dependence for the Helmholtz free energies, we have incorporated physicochemical effects explicitly as a perturbation in the adsorbed water chemistry. The microscopic counterpart of this procedure is the so-called *body force approach*.¹⁰ Within this framework the thermodynamics of a thin liquid film coating the mineral surfaces is altered to account for the excess intermolecular forces in terms of an extra body force term in the microscopic governing equations of the film. This extra component is related to the disjoining pressure¹¹ and appears thermodynamically defined at the microscale in terms of the change of free energy of the thin film with the thickness.⁹

The Coleman and Noll method^{2,3} is now used to exploit the restrictions placed by the entropy inequality (8) on the constitutive theory. To this end begin by expanding the material time derivatives $D_\alpha A_\alpha / Dt$ in terms of partial derivatives using the chain rule and the functional forms (12) and (13)

$$\sum_{\alpha=1,s} \phi_\alpha \rho_\alpha \frac{D_\alpha A_\alpha}{Dt} = \sum_{\alpha=1,s} \phi_\alpha \rho_\alpha \frac{\partial A_\alpha}{\partial T} \frac{DT}{Dt} + \phi_\alpha \rho_\alpha \frac{\partial A_\alpha}{\partial \mathbf{E}_s} : \frac{D_\alpha \mathbf{E}_s}{Dt} + \phi_\alpha \rho_\alpha \frac{\partial A_\alpha}{\partial \rho_\alpha} \frac{D_\alpha \rho_\alpha}{Dt}$$

where $A:B = \text{tr}(AB)$ for A and B symmetric tensors. Hence, introducing the thermodynamical pressures p_α

$$p_\alpha \equiv \rho_\alpha^2 \frac{\partial A_\alpha}{\partial \rho_\alpha}, \quad \alpha = 1, s \quad (14)$$

using the relations^{3,5}

$$\frac{D_s \mathbf{E}_s}{Dt} = \mathbf{F}_s^T \mathbf{d}_s \mathbf{F}_s, \quad \frac{D_1}{Dt} = \frac{D_s}{Dt} + \mathbf{v}_{1,s} \cdot \nabla \quad (15)$$

the constraint $\phi_1 + \phi_s = 1$ and the mass balance

$$\begin{aligned} \sum_{\alpha=1,s} \left(\frac{p_\alpha \phi_\alpha}{\rho_\alpha} \frac{D_\alpha \rho_\alpha}{Dt} + p_\alpha \phi_\alpha \operatorname{div} \mathbf{v}_\alpha \right) &= - \sum_{\alpha=1,s} p_\alpha \frac{D_\alpha \phi_\alpha}{Dt} = - p_1 \frac{D_1 \phi_1}{Dt} + (p_s - p_1) \frac{D_s \phi_1}{Dt} \\ &= - p_1 \mathbf{v}_{1,s} \cdot \nabla \phi_1 + (p_s - p_1) \frac{D_s \phi_1}{Dt} \end{aligned} \quad (16)$$

one obtains the expression

$$\begin{aligned} \sum_{\alpha=1,s} \phi_\alpha \rho_\alpha \frac{D_\alpha A_\alpha}{DT} - \sum_{\alpha=1,s} \phi_\alpha \rho_\alpha \frac{\partial A_\alpha}{\partial T} \frac{D_\alpha T}{Dt} - (\mathbf{t}_s^e + \mathbf{t}_s^l) : \mathbf{d}_s - \phi_1 \rho_1 \mathbf{v}_{1,s} \cdot \left(\frac{\partial A_1}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s \right) &= \frac{\phi_\alpha p_\alpha}{\rho_\alpha} \frac{D_\alpha \rho_\alpha}{Dt} \\ &= - \sum_{\alpha=1,s} p_\alpha \phi_\alpha \mathbf{I} : \mathbf{d}_\alpha - p_1 \mathbf{v}_{1,s} \cdot \nabla \phi_1 + (p_s - p_1) \frac{D_s \phi_1}{Dt} \end{aligned}$$

where $(\partial A / \partial \mathbf{E}) : \nabla \mathbf{E} = (\partial A / \partial E_{km}) E_{km,i}$ (with the repeated indices implying summation and comma denoting partial derivatives), $\mathbf{I} : \mathbf{d}_\alpha = \operatorname{div} \mathbf{v}_\alpha$ and the tensors \mathbf{t}_s^e and \mathbf{t}_s^l defined as

$$\mathbf{t}_s^e \equiv \rho_s \phi_s \mathbf{F}_s \frac{\partial A_s}{\partial \mathbf{E}_s} \mathbf{F}_s^T, \quad \mathbf{t}_s^l = \rho_1 \phi_1 \mathbf{F}_s \frac{\partial A_1}{\partial \mathbf{E}_s} \mathbf{F}_s^T \quad (17)$$

Using the above result the entropy inequality (8) can be rewritten as

$$\begin{aligned} T\Lambda &= \sum_{\alpha=1,s} - \phi_\alpha \rho_\alpha \left(\frac{\partial A_\alpha}{\partial T} + \eta_\alpha \right) \frac{D_\alpha T}{Dt} + \phi_1 (\mathbf{t}_1 + p_1 \mathbf{I}) : \mathbf{d}_1 \\ &\quad + (\phi_s \mathbf{t}_s + \phi_s p_s \mathbf{I} - \mathbf{t}_s^l - \mathbf{t}_s^e) : \mathbf{d}_s - \frac{1}{T} \nabla T \cdot \sum_{\alpha=1,s} \phi_\alpha \mathbf{h}_\alpha \\ &\quad - \mathbf{v}_{1,s} \cdot \left(\phi_1 \rho_1 \frac{\partial A_1}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s - p_1 \nabla \phi_1 + \hat{\mathbf{T}}_1 \right) + \frac{D_s \phi_1}{Dt} (p_1 - p_s) \geq 0 \end{aligned}$$

According to our constitutive assumptions, none of the constitutives functions of the set (11) depend on $\{D_\alpha T / Dt, \mathbf{d}_1$ and $\mathbf{d}_s\}$ and therefore the above indicates that Λ is a linear function of these quantities. Hence, the necessary and sufficient conditions for Λ to be non-negative for all possible processes, is that the coefficients of these variables must vanish. This gives the following relations which must always hold

$$\eta_\alpha = - \frac{\partial A_\alpha}{\partial T} \quad \alpha = 1, s \quad (18)$$

$$\phi_1 \mathbf{t}_1 = - \phi_1 p_1 \mathbf{I} \quad (19)$$

$$\phi_s \mathbf{t}_s = - \phi_s p_s \mathbf{I} + \mathbf{t}_s^e + \mathbf{t}_s^l \quad (20)$$

and leaves the dissipative residual inequality

$$T\Lambda = - \frac{1}{T} \nabla T \cdot \sum_{\alpha=1,s} \phi_\alpha \mathbf{h}_\alpha - \mathbf{v}_{1,s} \cdot \left(\phi_1 \rho_1 \frac{\partial A_1}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s - p_1 \nabla \phi_1 + \hat{\mathbf{T}}_1 \right) + \frac{D_s \phi_1}{Dt} (p_1 - p_s) \geq 0 \quad (21)$$

Equation (18) is a classical result stating that entropy and temperature and dual variables (e.g. Reference 39). Equation (19) states that the averaged (mesoscopic) adsorbed water stress tensor is a multiple of the identity. The physical meaning of the constitutive equation (20) for \mathbf{t}_s will be discussed next. In particular we shall illustrate that the components \mathbf{t}_s^e and \mathbf{t}_s^l in the r.h.s. denote, respectively, effective and physico-chemical stresses.

3. PHYSICAL INTERPRETATION OF THE NON-EQUILIBRIUM RESULTS

In order to provide an appropriate physical interpretation for the constitutive equation (20) for \mathbf{t}_s we pursue Murad and Cushman³⁰ who present an earlier physics interpretation of equation (20) for the isothermal case. Further we proceed by manipulating the energy equation to reach a desirable form to allow for interpretation of quantities such as intrinsic dissipation for swelling media.

3.1. Physical Interpretation of the tensor \mathbf{t}_s^l in terms of hydration stresses

Equation (20) is crucial in the present formulation since it contains important information on the constitutive behaviour of the solid-phase stress tensor for the swelling particles. Following Murad and Cushman,³⁰ introduce the total particle stress tensor \mathbf{t} and the particle thermodynamic pressure p ,

$$\mathbf{t} = \phi_s \mathbf{t}_s + \phi_l \mathbf{t}_l, \quad p = \phi_l p_l + \phi_s p_s \quad (22)$$

By adding (19) and (20) and using (22) we obtain

$$\mathbf{t} + p\mathbf{I} = \mathbf{t}_s^e + \mathbf{t}_s^l \quad (23)$$

The above result gives important insight into the stress in swelling particles. To elucidate this consider a fixed solid strain \mathbf{E}_s and then define the bulk phases B to be fluid unaffected by the solid phase (e.g. non-swelling granular media). By definition, the free energy of a bulk fluid A_B does not change with the proximity of the solid and therefore is independent of \mathbf{E}_s . Therefore from (17) \mathbf{t}_s^l is zero for a granular medium and \mathbf{t}_s^e remains unaltered as it only depends on the fixed solid strain \mathbf{E}_s . In this case (23) reduces to

$$\mathbf{t}_B + p_B \mathbf{I} = \mathbf{t}_s^e \quad (24)$$

where now the subscript B is used to denote the corresponding property for a non-swelling granular medium. In classical soil mechanics the above result resembles in form Terzaghi's effective stress principle at the mesoscale for non-swelling media with p_B and \mathbf{t}_s^e normally referred to as pore pressure (or bulk-phase pressure) and effective stress tensor, respectively. In classical stress analysis of non-swelling media, p_B has a definition analogous to p (22) except that it is equal to both the thermodynamic fluid and solid pressures (see e.g. References 40 and 22),

$$p_B = \phi_s p_s + \phi_l p_l = p_l = p_s \quad (25)$$

The effective stress tensor \mathbf{t}_s^e measures stresses induced by mineral to mineral contact and primarily controls the deformation of non-swelling systems such as sands, silts and low and medium plastic clays such as kaolinite or illite. The modified effective stress principle (23) for swelling media has the additional term \mathbf{t}_s^l , which is the stress due to the change in the free energy of the vicinal fluid with the strain of the mesoscale solid matrix. In contrast with coarse-grained soils where stress mechanisms are primarily controlled by the contact stresses \mathbf{t}_s^e , for swelling clays

such as montmorillonite the additional stress, \mathbf{t}_s^l , governs their deformation. Clearly, it is this additional term which accounts for the effects of the solid–fluid physico-chemical interactions and can be viewed as a stress structural component arising from surface hydration. Whence, as in Reference 29 we denote \mathbf{t}_s^l the *hydration stress tensor*. Recall that the thermodynamic definition of the effective stress tensor involves $\partial A_s/\partial \mathbf{E}_s$, whereas the hydration stress tensor involves $\partial A_1/\partial \mathbf{E}_s$. When surface hydration is the dominant component of physico-chemical forces, \mathbf{t}_s^l may be identified with the net attractive (*A*)-repulsive (*R*) forces between the clay particles, commonly denoted by (*R*–*A*) (see e.g. References 41–44 and 7). For a soil in which the solid phase is connected and for which there is no physico-chemical interaction between the solid and liquid phases, \mathbf{t}_s^l is zero. On the other hand, for a clay soil in which the solid minerals are highly ordered so that there is no solid–solid contact, \mathbf{t}_s^e is negligible, which means that straining the solid matrix does not change the energy of the solid A_s . Note that the partitioning of the total particle stress tensor \mathbf{t} into its effective, \mathbf{t}_s^e and hydration, \mathbf{t}_s^l , stress components differs from the what is presented by Lambe.⁴² In his work, it is assumed that only one overall stress exists in the particles, which is measured as the difference between the total macroscopic stress and bulk-phase pressure.

The thermodynamic definition ($\partial A_1/\partial \mathbf{E}_s$) of hydration stresses applies to the general adsorbed water concept as a vicinal fluid whose properties are perturbed by the deformation of the solid matrix. This definition incorporates both mobile and immobile phases. A sharper description of the mobile phase can be pursued if one excludes from the analysis the very low moisture content range of 1–10 monolayers by considering the adjacent fluid monolayers to the clay surface as part of the solid phase. Hence one can obtain a better portrait of the remaining mobile adsorbed water portion which is able to flow under a disjoining pressure gradient.¹¹ We shall henceforth restrict our analysis to a moderate moisture content range, which shall denote interlayer spacing occupied by 10–30 fluid monolayers. In this range, the adsorbed fluid exhibits fluid-like behaviour and, unlike the immobile phase, is not able to withstand shear stresses at equilibrium, only the normal hydrostatic swelling pressure. Thermodynamically, this assumption can easily be imposed by postulating that A_1 does not depend on the deviatoric part of the solid strain \mathbf{E}_s , but, unlike the bulk liquid, still depends on the volumetric strain, or on the volume fraction.

Let us henceforth consider that the microscopic solid phase is incompressible, i.e. ρ_s is constant. Let $\bar{\phi}_s = \bar{\phi}_s(\mathbf{X}_s)$ denote the volume fraction of the reference configuration and $J_s = \det \mathbf{F}_s$ be the Jacobian of the solid motion satisfying $J_s \phi_s = \bar{\phi}_s$.^{22,29} The Jacobian governs the volumetric mesoscopic deformation of the solid phase which is dictated by volume fraction changes since the platelets are assumed incompressible. In the range of moderate moisture content we assume that the free energy of the adsorbed fluid depends on volumetric strains by postulating $A_1 = A_1(J_s)$ or $A_1 = A_1(\phi_1)$ since they are coupled. Under this assumption definition (17) for \mathbf{t}_s^l may be simplified using the procedure of Murad and Cushman^{29,30} which consists of using (9) in (17) together with the identity $(\partial J_s^2/\partial \mathbf{C}_s)\mathbf{C}_s = J_s^2 \mathbf{I}$ ³⁵ and the above relation for J_s . We then have

$$\begin{aligned}\mathbf{t}_s^l &= 2\rho_1\phi_1\mathbf{F}_s\frac{\partial A_1}{\partial \mathbf{C}_s}\mathbf{F}_s^T = 2\rho_1\phi_1\frac{\partial A_1}{\partial J_s^2}\frac{\partial J_s^2}{\partial \mathbf{C}_s}\mathbf{C}_s = 2\rho_1\phi_1J_s^2\frac{\partial A_1}{\partial J_s^2}\mathbf{I} = 2\rho_1\phi_1J_s^2\frac{\partial A_1}{\partial \phi_s}\frac{\partial \phi_s}{\partial J_s^2}\mathbf{I} \\ &= -\frac{\rho_1\phi_1\bar{\phi}_s}{J_s}\frac{\partial A_1}{\partial \phi_s}\mathbf{I} = \rho_1\phi_1\phi_s\frac{\partial A_1}{\partial \phi_1}\mathbf{I}\end{aligned}$$

The above shows that in the range of moderate moisture contents ($25 \text{ \AA} < h < 75 \text{ \AA}$), the hydration stress tensor reduces to a multiple of the identity and consequently the only term in the r.h.s. of (23) with non-zero off-diagonal components capable of supporting shear stresses is

the effective stress tensor \mathbf{t}_s^e . Introducing the hydration pressure p_*

$$p_* = \rho_1 \frac{\partial A_1}{\partial \phi_1} \quad (26)$$

then the constitutive equation (17) for \mathbf{t}_s^l reduces to

$$\mathbf{t}_s^l = p_* \phi_1 \phi_s \mathbf{I} = p_* \phi_1 (1 - \phi_1) \mathbf{I} \quad (27)$$

The same procedure can be applied to simplify the middle term in the residual entropy inequality (21). We have

$$\rho_1 \phi_1 \frac{\partial A_1}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s = \rho_1 \phi_1 \frac{\partial A_1}{\partial \phi_1} \frac{\partial \phi_1}{\partial \mathbf{E}_s} : \nabla \mathbf{E}_s = \rho_1 \phi_1 \frac{\partial A_1}{\partial \phi_1} \frac{\partial \phi_1}{\partial \mathbf{E}_s} : \frac{\partial \mathbf{E}_s}{\partial \phi_1} \nabla \phi_1 = \rho_1 \phi_1 \frac{\partial A_1}{\partial \phi_1} \nabla \phi_1 = p_* \phi_1 \nabla \phi_1$$

Hence, in the range of moderate moisture content, the simplified version of the dissipative inequality (21) is

$$T\Lambda = -\frac{1}{T} \nabla T \cdot \sum_{\alpha=1,s} \phi_\alpha \mathbf{h}_\alpha - \mathbf{v}_{1,s} \cdot ((\phi_1 p_* - p_1) \nabla \phi_1 + \hat{\mathbf{T}}_1) + \frac{D_s \phi_1}{Dt} (p_1 - p_s) \geq 0 \quad (28)$$

3.2. Energy equation and dissipation

Since we have assumed that the clay minerals and adsorbed water are at local thermal equilibrium there is no need to consider individual energy balances for each phase. Rather, an energy equation for the mixture as a whole is considered by summing up the energy balances for the individual phases. Using the constraint (7) we have from (6)

$$\sum_{\alpha=1,s} \left(\phi_\alpha \rho_\alpha \frac{D_\alpha E_\alpha}{Dt} - \phi_\alpha \text{tr}(\mathbf{t}_\alpha \mathbf{d}_\alpha) + \text{div}(\phi_\alpha \mathbf{h}_\alpha) \right) + \hat{\mathbf{T}}_1 \cdot \mathbf{v}_{1,s} = \rho \hat{H}$$

where $\rho = \rho_1 \phi_1 + \rho_s \phi_s$. Since $E_\alpha = A_\alpha + T \eta_\alpha$ the above can be rewritten as

$$\sum_{\alpha=1,s} \left(\phi_\alpha \rho_\alpha \frac{D_\alpha A_\alpha}{Dt} + \phi_\alpha \rho_\alpha \eta_\alpha \frac{D_\alpha T}{Dt} \right) = \sum_{\alpha=1,s} \left(-\phi_\alpha \rho_\alpha T \frac{D_\alpha \eta_\alpha}{Dt} + \phi_\alpha \text{tr}(\mathbf{t}_\alpha \mathbf{d}_\alpha) - \text{div}(\phi_\alpha \mathbf{h}_\alpha) \right) - \hat{\mathbf{T}}_1 \cdot \mathbf{v}_{1,s} + \rho \hat{H} \quad (29)$$

By the chain rule, in the range of moderate moisture content, the expansions for $D_1 A_1 / Dt$ and $D_s A_s / Dt$ together with (18) and (26) are

$$\phi_1 \rho_1 \frac{D_1 A_1}{Dt} + \phi_1 \rho_1 \eta_1 \frac{D_1 T}{Dt} = \frac{\phi_1 p_1}{\rho_1} \frac{D_1 \rho_1}{Dt} + \phi_1 p_* \frac{D_1 \phi_1}{Dt} \quad (30)$$

$$\phi_s \rho_s \frac{D_s A_s}{Dt} + \phi_s \rho_s \eta_s \frac{D_s T}{Dt} - \mathbf{t}_s^e : \mathbf{d}_s = 0 \quad (31)$$

where $D_s \rho_s / Dt = 0$ since the solid was assumed incompressible. With ρ_s constant the overall mass balance (16) reduces to

$$\frac{\phi_1}{\rho_1} \frac{D_1 \rho_1}{Dt} = - \sum_{\alpha=1,s} \left(\phi_\alpha \text{div} \mathbf{v}_\alpha + \frac{D_\alpha \phi_\alpha}{Dt} \right) = - \sum_{\alpha=1,s} \phi_\alpha \text{div} \mathbf{v}_\alpha - \mathbf{v}_{1,s} \cdot \nabla \phi_1$$

By adding (30) and (31), using the above result and the second relation in (15) yields

$$\begin{aligned}
 \sum_{\alpha=1,s} \phi_{\alpha} \rho_{\alpha} \frac{D_{\alpha} A_{\alpha}}{Dt} + \sum_{\alpha=1,s} \phi_{\alpha} \rho_{\alpha} \eta_{\alpha} \frac{D_{\alpha} T}{Dt} - \mathbf{t}_s^e : \mathbf{d}_s &= \phi_1 \rho_* \frac{D_1 \phi_1}{Dt} + \frac{\phi_1 p_1}{\rho_1} \frac{D_1 \rho_1}{Dt} \\
 &= -p_1 \sum_{\alpha=1,s} \phi_{\alpha} \operatorname{div} \mathbf{v}_{\alpha} + \phi_1 p_* \frac{D_1 \phi_1}{Dt} - p_1 \mathbf{v}_{1,s} \cdot \nabla \phi_1 \\
 &= -p_1 \sum_{\alpha=1,s} \phi_{\alpha} \operatorname{div} \mathbf{v}_{\alpha} + \phi_1 p_* \frac{D_s \phi_1}{Dt} + (\phi_1 p_* - p_1) \mathbf{v}_{1,s} \cdot \nabla \phi_1
 \end{aligned} \quad (32)$$

In addition multiplying (19) and (20) by \mathbf{d}_{α} ($\alpha = 1, s$) and using (27) we have after adding them up

$$\begin{aligned}
 \sum_{\alpha=1,s} \phi_{\alpha} \mathbf{t}_{\alpha} : \mathbf{d}_{\alpha} - \mathbf{t}_s^e : \mathbf{d}_s &= - \sum_{\alpha=1,s} \phi_{\alpha} p_{\alpha} \mathbf{I} : \mathbf{d}_{\alpha} + \phi_s \phi_1 p_* \mathbf{I} : \mathbf{d}_s \\
 &= -p_1 \sum_{\alpha=1,s} \phi_{\alpha} \mathbf{I} : \mathbf{d}_{\alpha} + (p_1 - p_s) \phi_s \mathbf{I} : \mathbf{d}_s + p_* \phi_1 \phi_s \mathbf{I} : \mathbf{d}_s \\
 &= -p_1 \sum_{\alpha=1,s} \phi_{\alpha} \operatorname{div} \mathbf{v}_{\alpha} + (\phi_1 p_* + p_1 - p_s) \frac{D_s \phi_1}{Dt}
 \end{aligned} \quad (33)$$

where the mass balance for the incompressible solid

$$\frac{D_s \phi_1}{Dt} = \phi_s \operatorname{div} \mathbf{v}_s = \phi_s \mathbf{I} : \mathbf{d}_s$$

has been used in the last step. Combining (32) and (33) we get

$$\sum_{\alpha=1,s} \phi_{\alpha} \rho_{\alpha} \frac{D_{\alpha} A_{\alpha}}{Dt} + \sum_{\alpha=1,s} \phi_{\alpha} \rho_{\alpha} \eta_{\alpha} \frac{D_{\alpha} T}{Dt} = \sum_{\alpha=1,s} \phi_{\alpha} \mathbf{t}_{\alpha} : \mathbf{d}_{\alpha} - (p_1 - p_s) \frac{D_s \phi_1}{Dt} + (p_* \phi_1 - p_1) \mathbf{v}_{1,s} \cdot \nabla \phi_1$$

Using the above expression, the energy balance (29) reduces to

$$\sum_{\alpha=1,s} \phi_{\alpha} \rho_{\alpha} T \frac{D_{\alpha} \eta_{\alpha}}{Dt} + \operatorname{div}(\phi_{\alpha} \mathbf{h}_{\alpha}) - \rho \hat{H} = \Phi \quad (34)$$

where Φ denotes the intrinsic dissipation function

$$\Phi \equiv (p_1 - p_s) \frac{D_s \phi_1}{Dt} - (\hat{\mathbf{T}}_1 + (p_* \phi_1 - p_1) \nabla \phi_1) \cdot \mathbf{v}_{1,s} \quad (35)$$

Further, if we define the thermal dissipation function Φ_T by

$$\Phi_T \equiv -\frac{1}{T} \nabla T \cdot \sum_{\alpha=1,s} \phi_{\alpha} \mathbf{h}_{\alpha} \quad (36)$$

we have using (35), (36) in (28)

$$T\Lambda = \Phi + \Phi_T \geq 0$$

As usual, the entropy production is the sum of intrinsic and thermal dissipation functions. Note from (25) that in the case of a non-swelling granular media, $p_1 = p_s$ and therefore the first term in the r.h.s. of (35) vanishes. Consequently Φ has only one contribution due to the Darcy velocity $\mathbf{v}_{1,s}$. From (36), the non-equality between p_1 and p_s at non-equilibrium leads to the appearance of an additional component in the dissipation function.

4. EQUILIBRIUM THEORY

In this subsection we exploit the consequences of the entropy inequality at equilibrium

4.1. Equilibrium results

The state of thermodynamic equilibrium is defined to be the state at which $\{\mathbf{v}_{1,s}, D_s \phi_1 / Dt, \nabla T\}$ vanish. Following Callen³⁹ it is postulated that at equilibrium entropy is maximum and entropy generation is a minimum. To satisfy this latter requirement we must have $(\partial \Lambda / \partial z_a)_e = 0$ and $(\partial^2 \Lambda / \partial z_a \partial z_b)_e$ positive definite where z_a and z_b denote any of the above set of variables (see e.g. Reference 22). Application of these conditions to the residual entropy inequality (28) yields at equilibrium

$$\hat{\mathbf{T}}_1 = (p_1 - p_* \phi_1) \nabla \phi_1 \quad (37)$$

$$p_1 = p_s = p \quad (38)$$

$$\mathbf{h} \equiv \sum_{\alpha=1,s} \phi_\alpha \mathbf{h}_\alpha = \mathbf{0} \quad (39)$$

Equation (39) shows that the overall heat flux vanishes at equilibrium. Relation (38) states that at equilibrium, the thermodynamic pressures of the solid and adsorbed fluid phases are equal. Recall that this result reproduces (25) which is a result that has been extensively used for granular non-swelling media even away from equilibrium (see e.g. Reference 22). As we shall observe in next subsection the equality between p_1 and p_s may not necessarily hold for swelling systems undergoing non-equilibrium processes. Using (37)–(39) in (35) and (36) gives

$$\Lambda = \Phi_T = \Phi = 0$$

which reproduces the well-known result that the entropy production vanishes at equilibrium. Further, using (38) in (23) and (27) leads to the modified Terzaghi's principle at equilibrium

$$\mathbf{t} - \mathbf{t}_s^e = -(p_1 - p_* \phi_1 \phi_s) \mathbf{I}$$

We now exploit the consequences of (37). By combining this result with (19) and (5) we obtain at equilibrium

$$\nabla p_1 + p_* \nabla \phi_1 = 0 \quad (40)$$

Note from (40) that the pressure gradient is counter-balanced by a gradient in the volume fraction which implies that it is possible to have no flow even with a net pressure difference across the clay. To obtain further consequences, define the chemical potential (molar Gibbs free energy) μ_1 of the adsorbed water as

$$\mu_1 \equiv A_1 + \rho_1^{-1} p_1 \quad (41)$$

Hence, taking the gradient along with definitions (14), (18) and (26) for p_x , η_x and p_* we have by the chain rule

$$\nabla \mu_1 = \nabla \left(\frac{p_1}{\rho_1} \right) + \nabla A_1 = \nabla \left(\frac{p_1}{\rho_1} \right) + \frac{p_1}{\rho_1^2} \nabla \rho_1 - \eta_1 \nabla T + \frac{p_*}{\rho_1} \nabla \phi_1 = \frac{1}{\rho_1} (\nabla p_1 + p_* \nabla \phi_1) - \eta_1 \nabla T \quad (42)$$

Using (40) and recalling that $\nabla T = 0$ at equilibrium we get

$$\nabla \mu_1 = 0 \rightarrow \mu_1 = \text{const}$$

This is the well-known result that at equilibrium the chemical potential is constant.³⁹

4.2. Gibbs–Duhem Relation and the Excess $p_1 - p_B$

The fact that the chemical potential is constant at equilibrium has an important consequence. It allow us to quantify a new mesoscopic quantity inherent to swelling porous media: *the excess in adsorbed water pressure relative to the bulk-phase pressure*, $p_1 - p_B$, with p_B given as in (24), (25). This quantity measures a pressure excess due to the physico-chemical interaction between water and clay. In other words $p_1 - p_B$ would be zero if the properties of the water are unaffected by the interaction with the solid phase, as in the case of a bulk fluid. The excess $p_1 - p_B$ can be quantified by making use of the Gibbs–Duhem relation for the adsorbed fluid. In analogy with (42) we have by the chain rule.

$$d\mu_1 = -\eta_1 dT + \frac{1}{\rho_1}(dp_1 + p_* d\phi_1) \quad (43)$$

which represents the Gibbs–Duhem relation for the vicinal liquid. We make use of the above result to characterize a local reference bulk-phase pressure p_B . The reason for this characterization is because in Low's swelling pressure experiment of Figure 1, the reference bulk-phase pressure p_B is defined in the domain occupied by the bulk water. Therefore the generalization of definition (1) for Π to the case where particles undergo non-equilibrium processes requires a pointwise definition for the reference pressure $p_B(\mathbf{x}, t)$ holding in the particle domain. We shall construct this reference bulk water at instantaneous thermal and mechanical equilibrium with the adsorbed water such that their chemical potentials and temperatures are equal. Therefore setting $d\mu_1 = dT = 0$ in (43) yields $dp_1 = -p_* d\phi_1$. Further, recalling the volume fraction $\phi_1^* = e^*/(1 - e^*)$ defined in Low's relation (2) for which hydration and swelling forces are absent, for $\phi_1 = \phi_1^*$ water behaves as a bulk fluid and thus we have $A_1(\phi_1^*) = A_B$, where A_B denotes the free energy of the reference bulk fluid. Hence, integrating from ϕ_1 to ϕ_1^* along with the condition $p_1(\phi_1^*) = p_B$ gives

$$p_B = p_1 - \int_{\phi_1}^{\phi_1^*} p_*(s) ds \quad (44)$$

The above result furnishes the relation $p_B = p_B(p_1, \phi_1, \phi_1^*)$. Therefore, for given ϕ_1, p_1 and ϕ_1^* equation (44) can be used to characterize locally the reference bulk phase pressure p_B .

In addition, note that since p_1 affects the total particle thermodynamic pressure, p , through (22), we are also led to introduce an excess in total particle pressure p relative to the bulk phase p_B . Henceforth, we shall refer to this difference as an *excess in pore pressure*, (Π_B) , ie.,

$$\Pi_B \equiv p - p_B. \quad (45)$$

Similarly to the excess in fluid pressure $p_1 - p_B$ the above definition reflects locally the excess in pore pressure due to the physico-chemical interaction between the adsorbed water and the minerals. In other words, Π_B would be zero if the properties of the water are not perturbed by the presence of the platelets.

5. HMT SWELLING PRESSURE AND AN ALTERNATIVE FORM OF THE MODIFIED TERZAGHI'S EFFECTIVE STRESS PRINCIPLE

With the local reference bulk-phase pressure p_B characterized by (44) we may now pursue a generalized pointwise definition for the swelling pressure Π at non-equilibrium and also rewrite the modified Terzaghi's principle (23) in terms of p_B rather than p . For \mathbf{t} and \mathbf{t}_B given as in (23) and (24) define as Π

$$\Pi(\mathbf{x}, t)\mathbf{I} \equiv -(\mathbf{t} - \mathbf{t}_B) \quad (46)$$

Note that from (23), (24) and definition (45) the above r.h.s. reduces to $p - p_B - \phi_1\phi_s p_* = \Pi_B - \phi_1\phi_s p_*$ which shows that the swelling pressure is a scalar in the range of moderate moisture content. Hence, $\phi_1\phi_s p_*$ can also be interpreted as the difference $\Pi_B - \Pi$. The above definition aims to be consistent with Low's swelling pressure definition (1) valid only at equilibrium. Recall that for the well-ordered particle parallel platelet arrangement depicted in the swelling pressure experiment of Figure 1, $\mathbf{t}_s^e = 0$, $\mathbf{t}_B = -p_B\mathbf{I}$ and $\mathbf{t} = -P\mathbf{I}$ (P denotes the overburden pressure). Thus (46) reduces to the classical swelling pressure definition $\Pi = P - p_B$. Since $p_*\phi_1\phi_s = \Pi_B - \Pi$, in conjunction with (23) with (45) this shows

$$\mathbf{t} = -(p - p_*\phi_1\phi_s)\mathbf{I} + \mathbf{t}_s^e = -(p_B + \Pi - p_*\phi_1\phi_s)\mathbf{I} + \mathbf{t}_s^e = -(p_B + \Pi)\mathbf{I} + \mathbf{t}_s^e \quad (47)$$

Equation (47) consists of an alternative form of writing the mesoscopic modified effective stress principle with p replaced by p_B . In this case physico-chemical forces appeared measured by the swelling pressure Π . This alternative way of expressing the modified Terzaghi's principle resembles, in form some heuristic modified effective stress principles for clays discussed in for example References 41 and 42. Historically, physico-chemical forces have heuristically been modelled at the macroscale through the addition of a term to Terzaghi's principle which measures the effect of net repulsive (R) and attractive (A) forces between particles. This stress is commonly denoted by $(R - A)\mathbf{I}$ (see References 41 and 42). We then have

$$\mathbf{t} = -p_B\mathbf{I} + \mathbf{t}_s^e + (R - A)\mathbf{I} \quad (48)$$

Equation (47) is a first rational attempt for a rigorous derivation of the above heuristic modified Terzaghi's principle. When comparing (47) with (48) we have $R - A = -\Pi$ which shows that the net attractive-repulsive intra particles forces arising from hydration stresses are governed by the swelling pressure. Consequently some controversial aspects in stress analysis in cohesive soils may be elucidated within the current approach.

6. NEAR EQUILIBRIUM THEORY

In this section we linearize the dissipative inequality (28) about equilibrium to derive near-equilibrium results. We strictly linearize only about the one variable which gives a positive quadratic form in the entropy inequality. So for example, if z is a variable of the set $(\mathbf{v}_{1,s}, D_s\phi_1/Dt, \nabla T)$ which vanishes at equilibrium and f is the coefficient of z within the dissipative entropy inequality, the linearization procedure gives an approximation for the near-equilibrium value of f as, $f_{\text{neq}} \approx f_{\text{eq}} + C_z$ where C is the linearization constant. Our results are identified with a modified Darcy's law for the adsorbed water, a viscous non-equilibrium swelling pressure and Fourier's law of heat conduction. Moreover, we derive near equilibrium relations for the intrinsic and thermal dissipation functions.

6.1. Near-equilibrium results

By linearizing the dissipative inequality (28) about the variables $\{\mathbf{v}_{1,s}, D_s\phi_1/Dt, \nabla T\}$ one obtains

$$(p_*\phi_1 - p_1)\nabla\phi_1 + \hat{\mathbf{T}}_1 = -\mathbf{R}_1\mathbf{v}_{1,s} \quad (49)$$

$$p_1 - p_s = \mu_* \frac{D_s\phi_1}{Dt} \quad (50)$$

$$\mathbf{h} = -\mathbf{K}_T\nabla T \quad (51)$$

where \mathbf{R}_1 , \mathbf{K}_T and μ_* are material coefficients (the latter has dimensions of viscosity) which are constrained to be positive definite by the dissipative entropy inequality. Using (50) and (45) in (46) together with the second definition in (22) the near equilibrium relations for Π_B is

$$\Pi_B = p - p_B = \phi_s p_s + \phi_1 p_1 - p_B = \phi_s(p_s - p_1) + p_1 - p_B = \int_{\phi_1}^{\phi_1^*} p_*(s) ds - \phi_s \mu_* \frac{D_s\phi_1}{Dt} \quad (52)$$

In addition, we have for the swelling pressure

$$\Pi = \Pi_B - p_*\phi_1\phi_s = \int_{\phi_1}^{\phi_1^*} p_*(s) ds - p_*\phi_1\phi_s - \phi_s \mu_* \frac{D_s\phi_1}{Dt} \quad (53)$$

Using the above results in (23) and (22), the modified Terzaghi's principle near equilibrium is

$$\mathbf{t} - \mathbf{t}_s^e - p_*\phi_1\phi_s\mathbf{I} = -p\mathbf{I} = (-p_1 + \phi_s(p_1 - p_s))\mathbf{I} = \left(-p_1 + \mu_*\phi_s \frac{D_s\phi_1}{Dt}\right)\mathbf{I} \quad (54)$$

Note that even the solid is considered to be elastic *a priori*, the last term in the r.h.s. in (54) shows a viscoelastic behavior for the volumetric stresses.

6.2. Modified Darcy's law for the adsorbed water

Equation (49) is crucial as it leads to a modified form of Darcy's law for the vicinal fluid. Denoting $\mathbf{K}_1 = \phi_1^2 \mathbf{R}_1^{-1}$ the mesoscopic permeability tensor of the clay particles (recall that \mathbf{R}_1 is positive definite), using (19) and (49) in (5) and neglecting inertial effects we obtain the mesoscopic Darcy's law for the adsorbed water

$$\phi_1\mathbf{v}_{1,s} = -\mathbf{K}_1(\nabla p_1 + p_*\nabla\phi_1) \quad (55)$$

where $\mathbf{K}_1 = K_1\mathbf{I}$ for an isotropic medium. The first term on the r.h.s. of (55) leads to the traditional Darcy's law. The appearance of the last term confirms our expectation that since microscopic thin film flow under a thickness gradient, then analogously the averaged mesoscopic vicinal fluid will tend to flow from regions of high volume fraction to regions of low volume fraction. The appearance of this additional term is consistent with the fact that volume fraction gradients provide a potential for adsorbed water flow in a swelling medium. Note from (55) and (42) that under thermal equilibrium the driving force for vicinal fluid flow is the gradient of the chemical potential.

6.3. Viscoelasticity and relaxation

Equation (50) tells us that near equilibrium, the thermodynamic pressure of the adsorbed fluid and solid phases are not necessarily equal. Thus, the commonly assumed equality of p_l and p_s for granular non-swelling media (25) may not necessarily hold for swelling systems. The coefficient μ_* may be thought of as a relaxation factor which among other effects, accounts for the re-ordering of the adsorbed water, i.e. the redistribution of the fluid molecules over the interlamellar spaces as they are disturbed from the equilibrium state. Flow towards equilibrium is characterized by its specific time relaxation which depends on the size of the pores. For bulk fluids in macropores the relaxation time is usually much smaller than the macroscopic flow time.⁴⁵ It then follows that for a granular medium, $\mu_* \approx 0$, since there is very little re-ordering of the bulk liquid phase. On the other hand, the combination of physico-chemical forces and narrow pores increases the magnitude of the relaxation time of the vicinal fluid to the same order of the macroscopic flow. The evaluation of the coefficient μ_* requires experimental study, and most likely it varies depending on the composition and the interaction of the vicinal fluid and solid minerals. In Murad and Cushman,³⁰ μ_* was identified with the excess in the volumetric viscosity of the thin film relative to the bulk phase.

6.4. Fourier's law of heat conduction

Equation (51) is the classical Fourier's law of heat conduction for the overall heat flux. If the medium is isotropic, $\mathbf{K}_T = K_T \mathbf{I}$ where K_T is the thermal conductivity of the mixture given as

$$K_T = K_{Ts}(1 - \phi_l) + K_{Tl}\phi_l \quad (56)$$

with K_{Ts} and K_{Tl} denoting the corresponding thermal conductivities of the solid and fluid phases.

6.5. Intrinsic and thermal dissipations

Using (49)–(51) in (35) and (36) the near-equilibrium intrinsic and thermal dissipations for an isotropic swelling medium are

$$\Phi = \mu_* \left(\frac{D_s \phi_l}{Dt} \right)^2 + K_l |\mathbf{v}_{l,s}|^2, \quad \Phi_T = \frac{K_T}{T} |\nabla T|^2 \quad (57)$$

where $|\cdot|$ denotes the Euclidean norm. As explained earlier, in addition to the component arising from Darcy's velocity $\mathbf{v}_{l,s}$ the retardation factor μ_* plays a crucial role in the existence of an additional component in Φ which arises from the natural viscoelastic behaviour of the adsorbed water due to the redistribution of its molecules in the interlamellar spaces. Whence, physico-chemical forces in narrow pores contribute to an increase in the magnitude of the intrinsic dissipation Φ and to the entropy production.

7. TWO-SCALE LINEAR THERMOMECHANICAL MODEL

The two-scale infinitesimal theory for the clay particles is obtained following the standard linearization procedure. Consider that particles are initially in a homogeneous, equilibrium and isotropic state and assume small deformations and small deviations in temperature and adsorbed fluid density from their reference values. Expand A_α ($\alpha = l, s$) in a Taylor series in the vicinity of

equilibrium and retain quadratic terms in A_s and linear terms in the set of governing equations. Assume that A_s is an isotropic function of \mathbf{E}_s , depending only on its invariants to fulfill the usual objectivity requirements. The linearization procedure is exactly analogous to that of the classical linear isotropic thermoelasticity theory.³⁵ Consider that clay particles are initially at an equilibrium state given by $T = \bar{T}$, $\rho_1 = \bar{\rho}_1$, $\mathbf{E}_s = \mathbf{0}$, $\phi_1 = \bar{\phi}_1$ and $\phi_s = \bar{\phi}_s$ ($\bar{\phi}_s = 1 - \bar{\phi}_1$). Let \bar{A}_s , $\bar{\eta}_s$ and \bar{p}_1 denote the values of $\{A_s, \eta_s, p_1\}$ at the reference configuration. For simplicity assume initially a well ordered parallel platelet arrangement such that the reference configuration is free of effective stresses in the solid phase and consider that the only non-zero fluid stresses in the reference configuration are due to hydration stresses. Let $\{\bar{p}_*, \bar{K}_1, \bar{K}_T, \bar{\mu}'_*\}$ be the values of $\{p_*, K_1, K_T, \mu'_*\}$ at the reference configuration and let $\bar{\mu}_* \equiv \bar{\phi}_s \bar{\mu}'_*$. Further let the strain tensor be identified with its linearized form

$$\mathbf{E}_s = \nabla^s \mathbf{u}_s \quad (58)$$

where $\nabla^s \mathbf{u}_s = \frac{1}{2}(\nabla \mathbf{u}_s + \nabla \mathbf{u}_s^T)$, with \mathbf{u}_s denoting the displacement of the solid phase. Following the notation of thermoelasticity let $\theta \equiv T - \bar{T}$ and let A , Q , N and R denote the usual poroelastic coefficients in the sense of Biot⁴⁰ or Biot and Willis⁴⁶ which describe the linear behaviour of the isothermal porous medium in the absence of physico-chemical effects. For incompressible clay platelets $A = \lambda_s$ and $N = \mu_s$ where $\{\mu_s, \lambda_s\}$ denote the pair of Lamé coefficients of the platelet matrix. The coefficient R denotes the adsorbed water bulk modulus, given as $R = \phi_1/\beta_1$ where β_1 denotes the adsorbed water compressibility. Moreover, let $Q' = Q/\bar{\phi}_s$ and let α_s and C_s denote the coefficients of thermal expansion and the constant volume specific heat of the α -phase. Thus, we have the definitions

$$\beta_1 \equiv \frac{1}{\rho_1} \frac{\partial \rho_1}{\partial p_1} \bigg|_{\theta, \phi_1} \quad C_1 \equiv -\bar{T} \frac{\partial \eta_1}{\partial \theta} \bigg|_{\rho_1, \phi_1} \quad C_s \equiv -\bar{T} \frac{\partial \eta_s}{\partial \theta} \bigg|_{\mathbf{E}_s} \quad \alpha_s \equiv \frac{1}{3} \frac{\partial \text{tr } \mathbf{E}_s}{\partial \theta} \bigg|_{\text{tr } \mathbf{E}_s} \quad \alpha_1 \equiv -\frac{1}{\rho_1} \frac{\partial p_1}{\partial \theta} \bigg|_{p_1, \phi_1}$$

Further denote $K_s \equiv 3\lambda_s + 2\mu_s$ the solid matrix bulk modulus and γ the bulk modulus for physico-chemical stresses, defined as the coefficient of proportionality between p_* and ϕ_1 . Also introduce the physico-chemical coefficient of thermal expansion α_{1s} in the sense of Campanella and Mitchell⁴⁷ which accounts for changes in volume resulting from a temperature-induced change in physico-chemical forces. Within the current framework the new physico-chemical coefficients appear defined

$$\alpha_{1s} \equiv \frac{\partial \phi_1}{\partial \theta} \bigg|_{\rho_1, p_*} \quad \gamma = \bar{\phi}_1 \frac{\partial p_*}{\partial \phi_1}$$

Postulate the quadratic expansions

$$\begin{aligned} \rho_s \phi_s A_s &= \rho_s \bar{\phi}_s \bar{A}_s - \rho_s \bar{\phi}_s \bar{\eta}_s \theta + \frac{\lambda_s}{2} (\text{tr } \mathbf{E}_s)^2 + \mu_s \text{tr } \mathbf{E}_s^2 - (3\lambda_s + 2\mu_s) \alpha_s \text{tr } \mathbf{E}_s \theta - \frac{\rho_s C_s \bar{\phi}_s \theta^2}{2\bar{T}} \\ \rho_1 A_1 &= \bar{\rho}_1 \bar{A}_1 - \bar{\rho}_1 \bar{\eta}_1 \theta + \frac{\bar{p}_1}{\bar{\rho}_1} (\rho_1 - \bar{\rho}_1) + \bar{p}_* (\phi_1 - \bar{\phi}_1) + \frac{\gamma}{2\bar{\phi}_1} (\phi_1 - \bar{\phi}_1)^2 - \frac{\gamma \alpha_{1s}}{\bar{\phi}_1} (\phi_1 - \bar{\phi}_1) \theta - \frac{\bar{\rho}_1 C_1}{2\bar{T}} \theta^2 \\ &\quad + \frac{Q'}{\bar{\rho}_1 \bar{\phi}_1} (\phi - \bar{\phi}_1) (\rho_1 - \bar{\rho}_1) + \frac{\alpha_1}{\bar{\rho}_1 \beta_1} (\rho_1 - \bar{\rho}_1) \theta + \frac{1}{2\bar{\rho}_1^2 \beta_1} (\rho_1 - \bar{\rho}_1)^2 \end{aligned}$$

In the absence of physico-chemical effects, the above expansions reproduce those postulated by Schiffman³ for the linear thermoelastic case. Note that since the effective stresses are zero at the

reference configuration the expansions contain no linear term in \mathbf{E}_s , the above together with (14), (17) and (26) gives

$$\mathbf{t}_s^e = (\lambda_s \operatorname{tr} \mathbf{E}_s - K_s \alpha_s \theta) \mathbf{I} + 2\mu_s \mathbf{E}_s \quad (59)$$

$$p_1 = \bar{p}_1 + \frac{Q'}{\bar{\phi}_1} (\phi_1 - \bar{\phi}_1) + \frac{1}{\bar{\rho}_1 \bar{\beta}_1} (\rho_1 - \bar{\rho}_1) + \frac{\alpha_1}{\bar{\beta}_1} \theta \quad (60)$$

$$p_* = \bar{p}_* + \frac{\gamma}{\bar{\phi}_1} (\phi_1 - \bar{\phi}_1) + \frac{Q'}{\bar{\rho}_1 \bar{\phi}_1} (\rho_1 - \bar{\rho}_1) - \frac{\alpha_{1s} \gamma}{\bar{\phi}_1} \theta \quad (61)$$

In addition, using the aforementioned expansions for A_x in equation (18), gives the linearized entropy relations

$$\eta_s = \bar{\eta}_s + \frac{C_s}{\bar{T}} \theta + \frac{K_B \alpha_s}{\bar{\rho}_s \bar{\phi}_s} \operatorname{tr} \mathbf{E}_s \quad (62)$$

$$\eta_1 = \bar{\eta}_1 + \frac{C_1}{\bar{T}} \theta - \frac{\alpha_1}{\bar{\rho}_1^2 \bar{\beta}_1} (\rho_1 - \bar{\rho}_1) + \frac{\gamma \alpha_{1s}}{\bar{\rho}_1 \bar{\phi}_1} (\phi_1 - \bar{\phi}_1) \quad (63)$$

Equation (59) is the classical linear thermoelastic constitutive equation for the effective stresses. Equations (60) and (61) are linearized versions of the equations of state $p_1 = p_1(\theta, \rho_1, \phi_1)$ and $p_* = p_*(\theta, \rho_1, \phi_1)$. By linearizing $\mathbf{t}_s^l = \phi_s \phi_1 p_* \mathbf{I}$ we have from (61)

$$\mathbf{t}_s^l = p_* \phi_1 \phi_s \mathbf{I} = \left(\bar{p}_* \bar{\phi}_1 \bar{\phi}_s + \bar{f}(\phi_1 - \bar{\phi}_1) + \frac{Q' \bar{\phi}_s}{\bar{\rho}_1} (\rho_1 - \bar{\rho}_1) - \alpha_{1s} \gamma \bar{\phi}_s \theta \right) \mathbf{I},$$

$$\bar{f}(\bar{\phi}_1) \equiv \bar{\phi}_s \gamma + \bar{p}_* (\bar{\phi}_s - \bar{\phi}_1)$$

By neglecting all inertial and convective effects the linearized mass balances of adsorbed fluid and incompressible solid are

$$\frac{\bar{\phi}_1}{\bar{\phi}_s} \frac{\partial \phi_1}{\partial t} - \bar{\phi}_1 \operatorname{div} \frac{\partial \mathbf{u}_s}{\partial t} = 0 \quad (64)$$

$$\frac{\bar{\phi}_1}{\bar{\rho}_1} \frac{\partial \rho_1}{\partial t} + \frac{\partial \phi_1}{\partial t} + \bar{\phi}_1 \operatorname{div} \mathbf{v}_1 = 0 \quad (65)$$

After adding the above equations and rewriting the result in terms of Darcy velocity $\mathbf{q}_1 = \phi_1 \mathbf{v}_{1,s}$ we have

$$\frac{\bar{\phi}_1}{\bar{\rho}_1} \frac{\partial \rho_1}{\partial t} + \operatorname{div} \mathbf{q}_1 + \operatorname{div} \frac{\partial \mathbf{u}_s}{\partial t} = 0$$

In addition, using equations (62) and (63) and the mass balance (64) in the linearized energy equation (34) gives, neglecting convective effects

$$\begin{aligned} \operatorname{div} \mathbf{h} - \Phi - \bar{\rho} \hat{H} &= -T \sum_{\alpha=1,s} \bar{\phi}_\alpha \bar{\rho}_\alpha \frac{\partial \eta_\alpha}{\partial t} = -\bar{\rho} C \frac{\partial \theta}{\partial t} - \alpha_{1s} \bar{T} \gamma \frac{\partial \phi_1}{\partial t} - \bar{T} K_s \alpha_s \frac{\partial \operatorname{div} \mathbf{u}_s}{\partial t} + \frac{\bar{T} \alpha_1 \bar{\phi}_1}{\bar{\rho}_1 \bar{\beta}_1} \frac{\partial \rho_1}{\partial t} \\ &= -\bar{\rho} C \frac{\partial \theta}{\partial t} - \bar{T} (\alpha_{1s} \gamma \bar{\phi}_s + K_s \alpha_s) \frac{\partial \operatorname{div} \mathbf{u}_s}{\partial t} + \frac{\bar{T} \alpha_1 \bar{\phi}_1}{\bar{\rho}_1 \bar{\beta}_1} \frac{\partial \rho_1}{\partial t} \end{aligned}$$

where

$$\bar{\rho}C = \rho_s \bar{\phi}_s C_s + \bar{\rho}_1 \bar{\phi}_1 C, \quad \bar{\rho} = \rho_s + \bar{\rho}_1$$

The last three terms of the r.h.s. measure, respectively, the mechanical work associated to hydration, effective stress and fluid compressibility.

7.1. Linearized thermoviscoelastic governing equations

Let Ω_1 be the clay particle domain. With \mathbf{E}_s and Φ given as in (58) and (57), respectively, our mesoscopic linearized governing equations are

Mass of the solid phase

$$\frac{\partial \phi_1}{\partial t} - \bar{\phi}_s \operatorname{div} \frac{\partial \mathbf{u}_s}{\partial t} = 0 \quad (66)$$

Total mass:

$$\bar{\phi}_1 \frac{\partial \rho_1}{\partial t} + \bar{\rho}_1 \left(\operatorname{div} \mathbf{q}_1 + \operatorname{div} \frac{\partial \mathbf{u}_s}{\partial t} \right) = 0 \quad (67)$$

Total momentum:

$$\operatorname{div} \mathbf{t} = 0$$

Total particle stress constitutive equation:

$$\mathbf{t} = -p_1 \mathbf{I} + \mathbf{t}_s^e + \left(\phi_1 \phi_s p_* + \bar{\mu}_* \frac{\partial \phi_1}{\partial t} \right) \mathbf{I} \quad (68)$$

Linearized effective stress constitutive relation:

$$\mathbf{t}_s^e = (\lambda_s \operatorname{div} \mathbf{u}_s - \alpha_s K_s \theta) \mathbf{I} + 2\mu_s \nabla^s \mathbf{u}_s \quad (69)$$

Linearized hydration stress constitutive relation:

$$\phi_1 \phi_s p_* = \bar{p}_* \bar{\phi}_1 \bar{\phi}_s + \bar{f}(\phi_1 - \bar{\phi}_1) + \frac{Q' \bar{\phi}_s}{\bar{\rho}_1} (\rho_1 - \bar{\rho}_1) - \alpha_{1s} \gamma \bar{\phi}_s \theta \mathbf{I} \quad (70)$$

Modified Darcy's law for the adsorbed water:

$$\mathbf{q}_1 = -\bar{K}_1 (\nabla p_1 + \bar{p}_* \nabla \phi_1) \quad (71)$$

Energy equation for the mixture:

$$\operatorname{div} \mathbf{h} - \bar{\rho} \hat{H} - \Phi = -\bar{\rho} C \frac{\partial \theta}{\partial t} - \bar{T} (\alpha_{1s} \gamma \bar{\phi}_s + K_s \alpha_s) \operatorname{div} \frac{\partial \mathbf{u}_s}{\partial t} + \frac{\bar{T} \alpha_1 \bar{\phi}_1}{\bar{\rho}_1 \beta_1} \frac{\partial \rho_1}{\partial t}$$

Fourier's law of heat conduction:

$$\mathbf{h} = -\bar{K}_T \nabla \theta \quad (72)$$

Linearized equation of state of the adsorbed water:

$$p_1 = \bar{p}_1 + \frac{Q'}{\bar{\phi}_1} (\phi_1 - \bar{\phi}_1) + \frac{1}{\bar{\rho}_1 \beta_1} (\rho_1 - \bar{\rho}_1) + \frac{\alpha_1}{\beta_1} \theta \quad (73)$$

For given sets of thermomechanical coefficients $\{\lambda_s, \mu_s, \alpha_s, \bar{K}_1, \bar{K}_T, C, \alpha_1, \beta_1, Q'\}$ and physico-chemical parameters $\{\bar{f}, \bar{p}_*, \alpha_{1s}, \gamma, \bar{\mu}_*\}$, the above system of governing equations, formulated in terms of the unknowns $\{\rho_1, \mathbf{u}_s, \mathbf{q}_1, \mathbf{t}_s^e, \phi_1, p_*, p_1, \mathbf{t}, \theta, \mathbf{h}\}$, governs hydration swelling of the clay particles. The resultant system exhibits a structure similar to those governing thermoelastic consolidation of granular media and exhibit additional physico-chemical and viscous-type terms accounting for the thermal physico-chemical interaction between the adsorbed fluid and the clay minerals. An important consequence of the model proposed herein is the reproduction of the classical linear model of thermoelastic consolidation (see e.g. Reference 12) upon neglect of the physico-chemical parameters.

Finally, we remark that experimental information on the hydration pressure \bar{p}_* can be obtained by pursuing the approach of Murad and Cushman³⁰ which consists in deriving an equilibrium relationship between p_* and Π and use Low's experimental result (2) to evaluate the relation $\Pi = \Pi(\phi_1)$ and consequently obtain indirectly the constitutive relation $p_* = p_*(\phi_1)$.

8. CONCLUSIONS

A two-scale thermomechanical model of two-phase 2-1 lattice swelling clays composed of adsorbed water and clay minerals is presented using a hybridization of the mixture-theoretic approach of Bowen.⁴⁸ By exploiting the entropy principle within the Coleman and Noll method constitutive results which captured the physics of swelling were derived in a unified manner.

The most critical step in the analysis was to provide the set of independent constitutive variables for the solid and adsorbed liquid phases. We showed that postulating the dependence of the free energy of the adsorbed water on the volume fraction and including the volume fraction gradient in the set of independent constitutive variables plays a critical role in swelling colloids. For example, the inclusion of these variables led to the appearance of additional hydration stresses which account for physico-chemical effects. In the proposed formulation hydration effects are manifest in the appearance of additional terms in the two-scale governing equations, in particular: (1) In a modified effective stress principle for swelling porous media which incorporates the hydration stress tensor \mathbf{t}_s^1 . (2) In the energy balance where physico-chemical effects are manifest through an additional term accounting for the mechanical work of hydration stresses. (3) In the appearance of an additional physico-chemical coefficient of thermal expansion of the platelet matrix α_{1s} . (4) In a modified form of Darcy's law governing the vicinal water flow which involves an additional volume fraction gradient accounting for the hydrophilicity between adsorbed water and the clay minerals. (5) In the appearance of a retardation viscosity coefficient (μ_*) which led to a viscoelastic behaviour coelastic effect also led to the appearance of an additional viscous component in the intrinsic dissipation function in the energy equation.

Further work is under progress to analyse extensions of the proposed model to more complex constitutive behaviour such as plasticity and heat-induced moisture movement. In both cases extensions can be obtained by adding internal variables to the set of independent variables in the hybrid mixture theory (plastic deformation and moisture content). In the former case the development of a comprehensive theory for inelastic soils with physico-chemical effects can be

obtained by coupling the proposed approach with the thermodynamical framework developed by Modaressi and Laloui⁴⁹ for the Cam-Clay model.

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